SHOBHIT NIRWAN'S

ORGANIC CHEMISTRY SOME BASIC PRINCIPLES & TECHNIQUES

Organic Chemistry an Introduction

Tetravalence of carbon: shapes of organic compounds.

- The shapes of carbon compounds.
- Some characteristic features of π bonds.

Structures representations of organic compounds.

(i) complete, condensed and bond line structural formula.

(ii) Three-dimensional representation of organic molecules

Classification of organic compounds.

(i) Acyclic or open-chain compounds

(ii) Alicyclic or closed chain or ring compounds.

(iii) Aromatic Compounds

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(b) Non- Benzenoid Compounds

(c) Heterocyclic Aromatic Compound

(d) Functional Compounds

(e) Homologous Series

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- Structural Isomerism
- Stereoisomerism

Nomenclature of Organic compounds.

(i) The IUPAC system of nomenclature

(ii) IUPAC nomenclature of alkanes

(iii) Nomenclature of organic compounds having functional group(s)

(iv) Nomenclature of substituted Benzene compounds

Fundamental concepts in the organic reaction mechanism

(i) Fission of a covalent bond

(ii) Nucleophiles and Electrophiles

(iii)Electron movement in organic reactions

(iv)Electron displacement effects in covalent bonds.

(v) Inductive effect

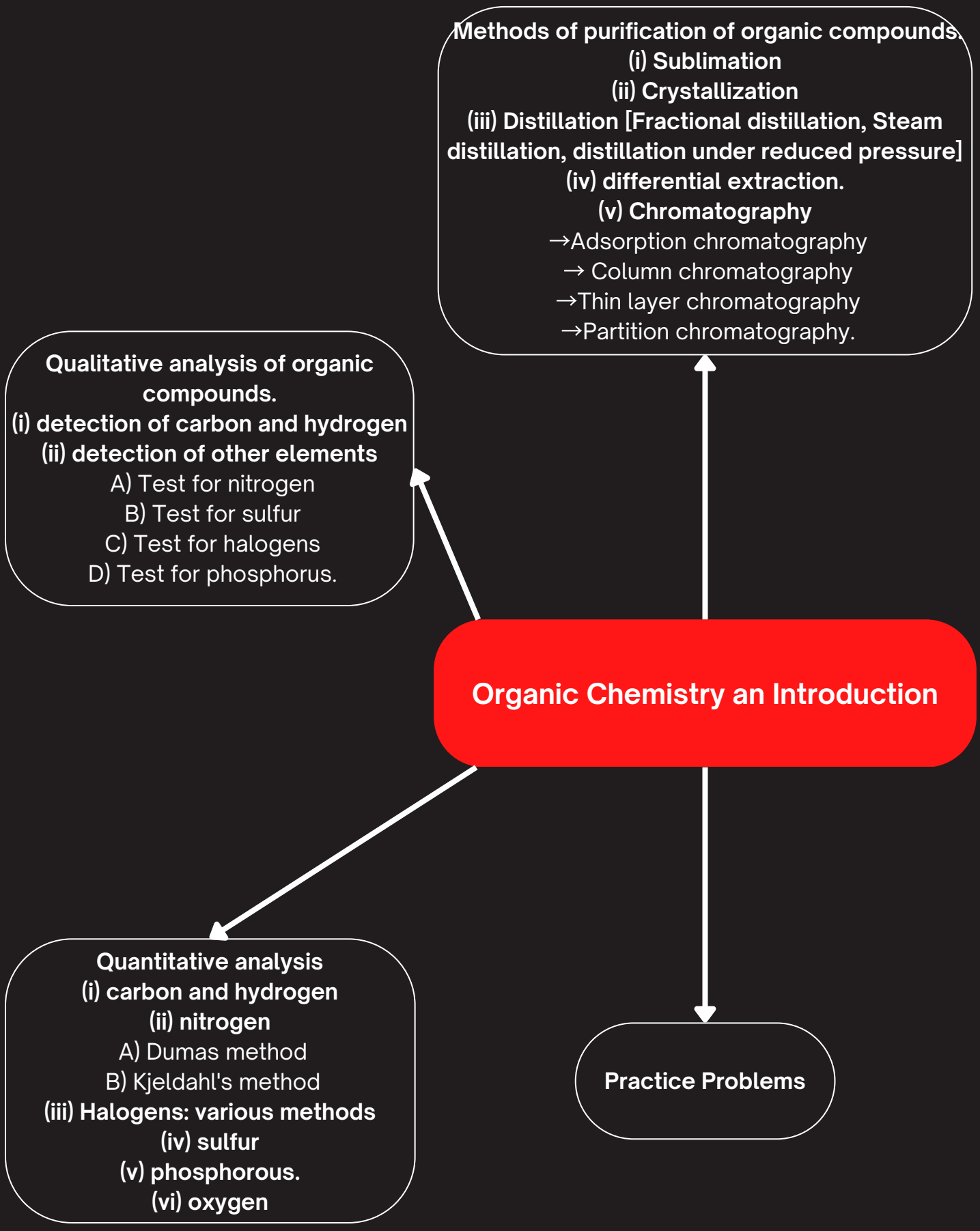
(vi) Resonance structure

(vii) Resonance effect (+R effect , -R effect)

(viii) Electromeric effect (E effect)

(ix) Hyperconjugation

(x) Types of organic reactions and mechanisms.


Methods of purification of organic compounds.
(i) Sublimation
(ii) Crystallization
(iii) Distillation [Fractional distillation, Steam distillation, distillation under reduced pressure]
(iv) differential extraction.
(v) Chromatography
→Adsorption chromatography
→ Column chromatography
→Thin layer chromatography
→Partition chromatography.
Qualitative analysis of organic compounds.
(i) detection of carbon and hydrogen
(ii) detection of other elements
A) Test for nitrogen
B) Test for sulfur
C) Test for halogens
D) Test for phosphorus.
Organic Chemistry an Introduction
Quantitative analysis
(i) carbon and hydrogen
(ii) nitrogen
A) Dumas method
B) Kjeldahl's method
(iii) Halogens: various methods
(iv) sulfur
(v) phosphorous.
(vi) oxygen
Practice Problems

GENERAL INTRODUCTION

- Carbon एक ऐसा element हैजि सके पास catenation (खदुके साथी bond बनाना) की property है, जि स वजह से carbon covalent bond बनाता हैदसु रे carbon के साथ l
- Carbon दसु रे elements (oxygen , nitrogen , sulphur , phosphorous and halogens) के साथ भी covalent bond बनाता हैंऔर compound form करता हैं और इन्ही को हम organic compounds कहतेहैंl
- इन्ही सब compounds के बारेमेंहम organic chemistry के अदं र पढतेहैं
- Organic compounds are involved in deoxyribonucleic acid (DNA) and proteins. That is in our blood, muscles, and skin
- Organic chemicals are in materials like clothing, fuels, polymers, dyes, and medicines.
- पहले माना जाता था की organic compounds are obtained from plants and animals and inorganic compounds are prepared from mineral sources.
- बाद में एक scientist ने prove कि या कि organic compounds urea formed from an inorganic compound(ammonium cyanate)

$$\underset{\text{Ammonium Cyanate}}{NH_4CNO} \xrightarrow{\text{Heat}} \underset{\text{Urea}}{NH_2CONH_2}$$

- Later acetic acid synthesis by Kolbe and of methane by Berthelot theat organic compound can be synthesized from inorganic sources in laboratory.

TETRAVALENCE OF CARBON: SHAPES OF ORGANIC COMPOUNDS:

(i) The shapes of carbon compounds:

- Hybridization gives us an idea of bond length and bond enthalpy (bond कितना strong हैं)

- **Sp** (s= 50% ,p= 50%): contains more S character hence is closer to its nucleus.
  ∴ Forms a shorter and strong bond

- **Sp3** (s= 25% , p= 3x25%) : contains less S character
  ∴ forms a weaker bond compared to Sp

- **Sp2:** length , bond enthalpy और S character में Sp और Sp3 के बीच मेंहैं।
- ये बात ध्यान में रखे की अगर hybridisation में कुछ change होगा तो वो Carbon की electronegativity पे effect करेगा । तो जिसमें S character ज्यादा होगा उस्का electronegativity ज्यादा होगा ।

- **Electronegativity order : Sp > sp2> sp3**

Some characterisitic features of pi bonds

π bond :

- the parallel orientation of 2p orbitals.
- sideways overlap
- P orbitals एक दसरे से parallel होगा और plane से perpendicular होगा ।
- C = C का rotation नहीं हो सकता (rotation is restricted)
- electron charge cloud π bond का plane के ऊपर और नीचे located होगा । इसिलिये electron easily available हैं attacking reagents के लियेा

∴ π bonds provide the most reactive centers in the molecules containing multiple bonds.

Q1)How many σ and π bonds are present in each of the following molecules?
(a) HC≡CCH=CHCH3
(b) CH2=C=CHCH3

Solution
(a) σC – C: 4; σC–H : 6; πC=C :1; π C≡C:2
(b) σC – C: 3; σC–H: 6; πC=C: 2

Q2)What is the type of hybridisation of each carbon in the following compounds?
(a) CH3Cl, (b) (CH3)2CO, (c) CH3CN,(d) HCONH2, (e) CH3CH=CHCN

Solution
(a) sp3, (b) sp3 sp2, (c) sp3, sp, (d) sp2, (e) sp3, sp2, sp2sp

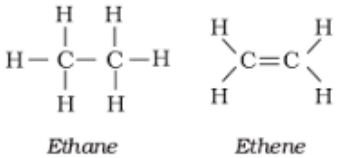
Q3)Write the state of hybridization of carbon in the following compounds and shapes of each of the molecules.
(a) H2C=O, (b) CH3F, (c) HC≡N.

Solution
(a) sp2 hybridised carbon, trigonal planar
(b) sp3 hybridized carbon, tetrahedral
(c) sp hybridized carbon, linear.

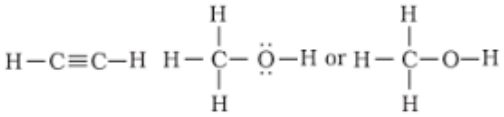
Structural Representation of Organic Compounds

(i) Complete , condensed and bond–line structural formulas

- The lewis structure or dot structure, condensed structure, and bond line structural formulas are some of the specific types
- Lewis structure को हम simplify कर सकतेहैं2 electron covalent bond by a dash (-) के formमेंl
- **Single dash = single bond (-)**
- **Double dash = double bond (=)**
- **Triple bond = triple bond (≡)**
- lone pair of electrons on heteroatoms (eg: oxygen, nitrogen, sulfur, halogens, etc) may or may not be shown.
- Complete structural formulas


Ethane

Ethene


Ethyne

Methanol

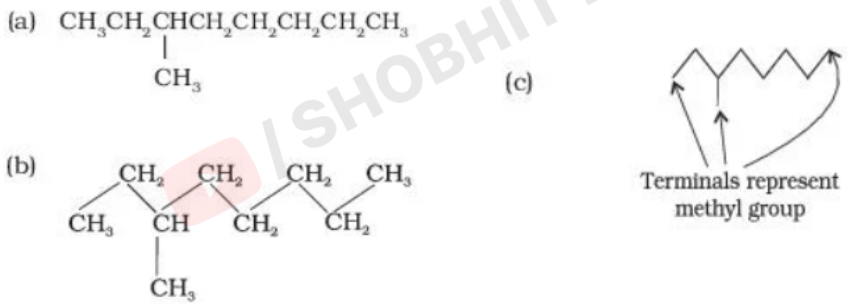
- **Condensed structural formula**:सारे dashes जो covalent bond represent करते हैं वो हटा दो

CH3CH3	H2C = CH2	HC ≡ CH	CH3 OH
Ethane	ethene	ethyne	methanol

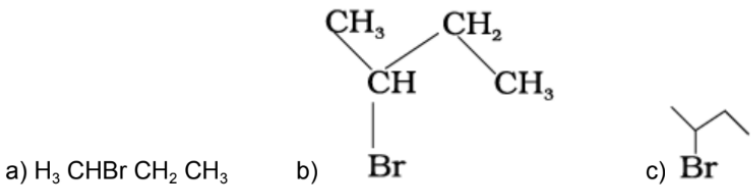
- **CH3CH2CH2 CH2CH2 CH2CH3 can be further condensed to CH3(CH2)6CH3**

Bond line structural formula

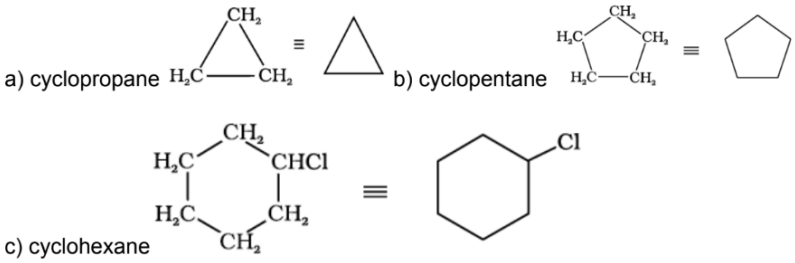
- In Structures in which only lines are used, carbon and hydrogen atoms are not shown.
- Lines representing carbon–carbon bonds are drawn in a zig – zag
- fashion.
- Only specific atoms like oxygen, chlorine, nitrogen, etc are written
- Terminal denotes methyl (-CH3) groups unless indicated by a functional group.
- Line junctions (जहां दो अलग अलग line मिल रहेहैं) denote carbon atoms bonded appropriate no of hydrogens required to satisfy the valency of the carbon atoms.
- Eg: various ways to represent 3 – Methyloctane



Various ways of representing 2-bromobutane



Some cyclic Compounds

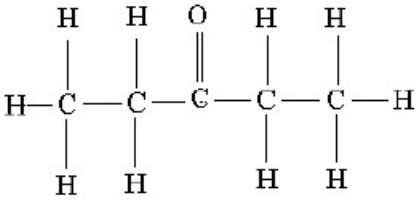


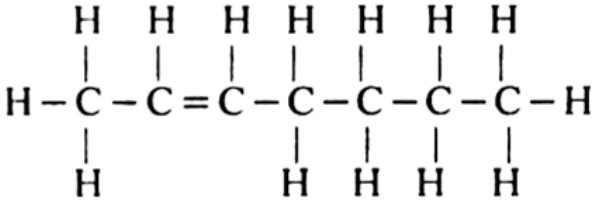
Q4)Expand each of the following condensed formulas into their complete structural formulas.

(a) CH3CH2COCH2CH3

(b) CH3CH=CH(CH2)3CH3

Solution

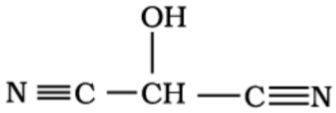




Q5)For each of the following compounds, write a condensed formula and also their bond-line formula.

(a) HOCH2CH2CH2CH(CH3)CH(CH3)CH3

(b)



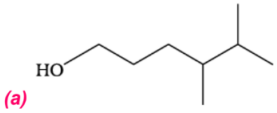
Solution:

Condensed formula:

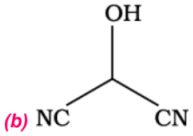
(a) HO(CH2)3CH(CH3)CH(CH3)2

(b) HOCH(CN)2

Bond-line formula:



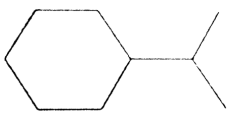
(a)



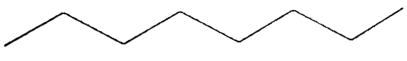
(b)

Q6)Expand each of the following bond-line formulas to show all the atoms including carbon and hydrogen

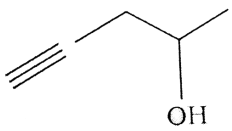
(a)



(b)



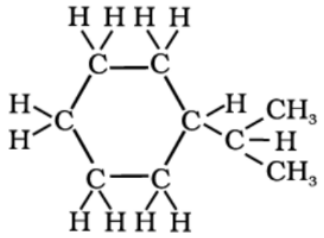
(c)



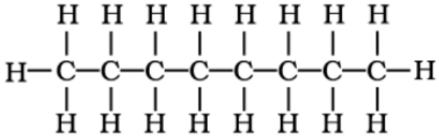
(d)

Solution

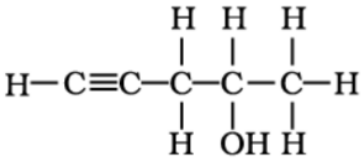
(a)



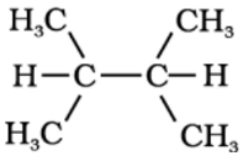
(b)



(c)



(d)



Three Dimensional representation of organic molecules:

- **Solid Wedge**() → indicates a bond projecting out of the plane of the paper and towards the observer.
- **Dashed wedge** ()→ indicates the bond projecting out of the plane and away from the observer.
- **Normal line(-)**: indicates bond lying in the plane of the paper

Molecular models: (green box in NCERT)

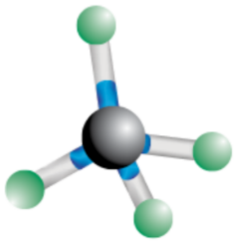
- Physical devices for better visualization of #-D shapes organic molecules.
- made up of wood, plastic, or metal.
- There are 3 types:

1. Framework model:

(i) bonds connecting the atoms of a molecule and not the atoms.
(ii) they are shown
(iii) this model shows pattern of bonds and ignores the size of atoms.

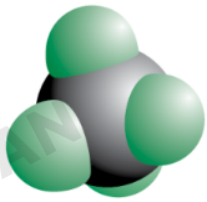
2.) Ball and stick model

- both the atoms of the bonds are shown, balls represent atoms, and stick denote a bond
- if sticks are replaced by springs then it is called ball spring model.

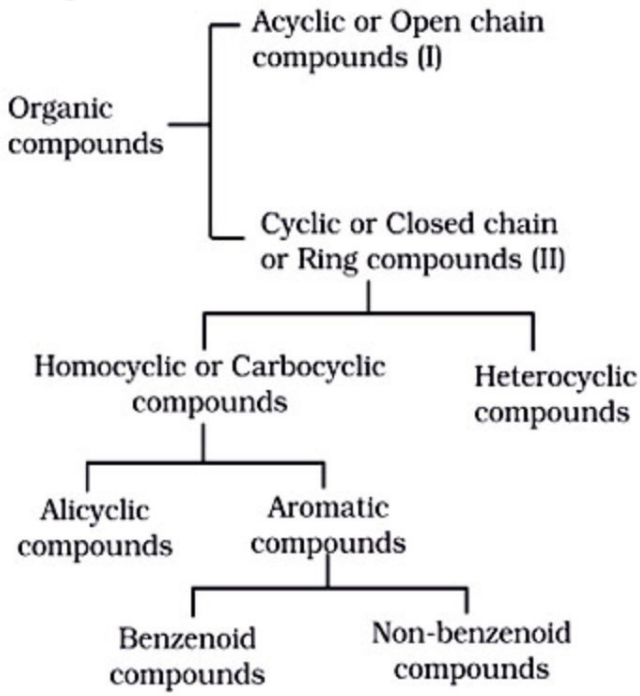


3.) Space filling model

- this model represents the relative size of each atom based on the van der Waals radius.
- bonds are not shown in this model, showing the volume occupied by each atom in the molecule.

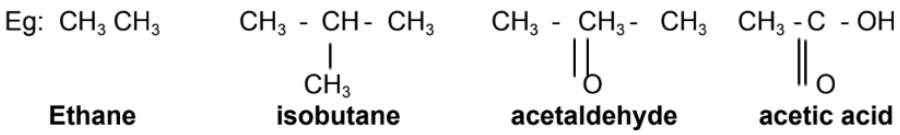


Classification of compounds



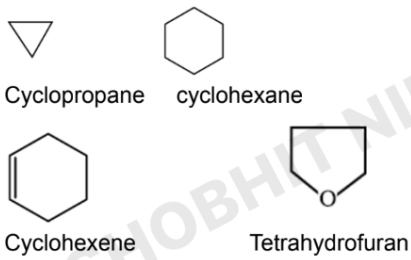
(i) Acyclic or open-chain compounds:

- Also called aliphatic compounds.
- Consist of straight or branched chain compound.



(ii) Alicyclic or closed chain or ring compounds:

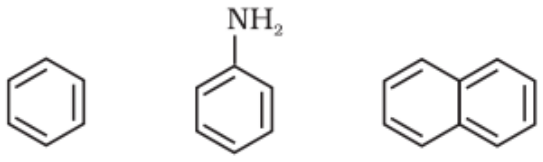
- Alicyclic (aliphatic cyclic) contains carbon atoms joined in the form of a ring (homocyclic)
- atoms other than carbon are also present in the ring (heterocyclic)



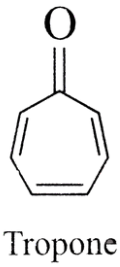
(iii) Aromatic compounds:

- Include benzene and other related ring compounds (benzenoid)
- May have hetero atom in the ring (heterocyclic aromatic compounds)

a) Benzenoid aromatic compounds

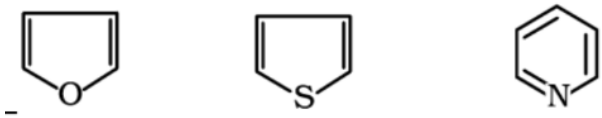


b) Non-benzenoid compound



Tropone

c) Heterocyclic aromatic compounds



d) Functional Group- Defined as an atom or group of atoms joined in a specific manner that is responsible for the characteristic chemical properties of the organic compounds.
Eg: hydroxyl group (-OH) , aldehy- de group (-CHO) and carboxylic acid group (-COOH) etc.

(e) Homologous series:
1. A group or a series of organic compounds each containing a functional group forms a homologous series and the members of the series are called homologous.

2. Members are represented by general molecular formulas and the successive
members differ from each other in the molecular formula by a –CH_2 unit.

Eg examples of homologous series: alkanes, alkenes, alkynes, haloalkanes,alkanols, alkanals , alkanones, alkanoic acids,amines etc.

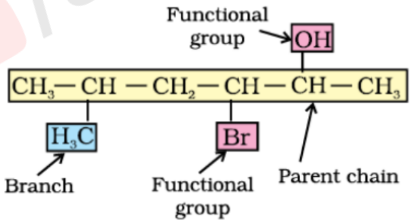
Nomenclature of Organic compounds

- IUPAC (international union of pure and applied chemistry) systematic method of naming
- Common names: citric acid (as found in citrus fruits) trisal names formic acid (found in red ant , latin word for ant formica), buckminsterfullerene (C60 – cluster – form of carbon)

Compound	Common name
CH_4	Methane
$H_3CCH_2CH_2CH_3$	*n*-Butane
$(H_3C)_2CHCH_3$	Isobutane
$(H_3C)_4C$	Neopentane
$H_3CCH_2CH_2OH$	*n*-Propyl alcohol
HCHO	Formaldehyde
$(H_3C)_2CO$	Acetone
$CHCl_3$	Chloroform
CH_3COOH	Acetic acid
C_6H_6	Benzene
$C_6H_5OCH_3$	Anisole
$C_6H_5NH_2$	Aniline
$C_6H_5COCH_3$	Acetophenone
$CH_3OCH_2CH_3$	Ethyl methyl ether

(i) The IUPAC System of Nomenclature:

- Name is derived by identifying the parent hydrogen and functional group(s) attached to it.



(By using prefixes (placed before any other word) and suffixes (placed after another word) parent name can be modified.

- **Hydrocarbon: → Compounds containing carbon and hydrogen only .**

→ **Saturated hydrocarbon:** contains only carbon–carbon single bonds.
Eg: alkane, were known as paraffin earlier.

→ **Unsaturated hydrocarbon:** contain at least one carbon–carbon double or triple bond.

(ii) IUPAC nomenclature of alkanes:

(a) Straight chain hydrocarbons:

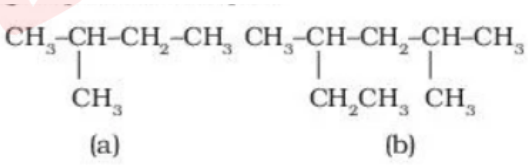
- Names are based on their chain structure
- End with the suffix - `ane', prefix – indicate. no carbon atoms are present in the chain (except from CH4 to C4H10 as their names are derived from trivial/common names)

Name	Molecular formula	Name	Molecular formula
Methane	CH_4	Heptane	C_7H_{16}
Ethane	C_2H_6	Octane	C_8H_{18}
Propane	C_3H_8	Nonane	C_9H_{20}
Butane	C_4H_{10}	Decane	$C_{10}H_{22}$
Pentane	C_5H_{12}	Icosane	$C_{20}H_{42}$
Hexane	C_6H_{14}	Triacontane	$C_{30}H_{62}$

(b) Branched-chain hydrocarbons:

- Small chains of carbon atoms are attached at one or more carbon atoms of the parent chain.
- Small carbon chains are called althyl groups.

Name of alkyl groups are prefix to the name of parent alkane.



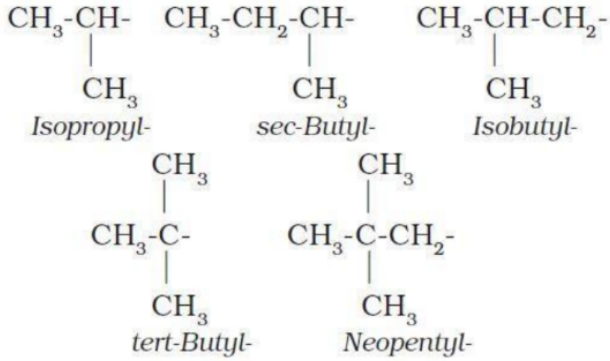
Q7) How is alkyl group derived?

Solution: Derived from a saturated hydrocarbon by removing a hydrogen atom from carbon i.e CH4 becomes CH3 (methyl group) `ane' is substituted by `yl'

Alkane		Alkyl group	
Molecular formula	Name of alkane	Structural formula	Name of alkyl group
CH_4	Methane	$-CH_3$	Methyl
C_2H_6	Ethane	$-CH_2CH_3$	Ethyl
C_3H_8	Propane	$-CH_2CH_2CH_3$	Propyl
C_4H_{10}	Butane	$-CH_2CH_2CH_2CH_3$	Butyl
$C_{10}H_{22}$	Decane	$-CH_2(CH_2)_8CH_3$	Decyl

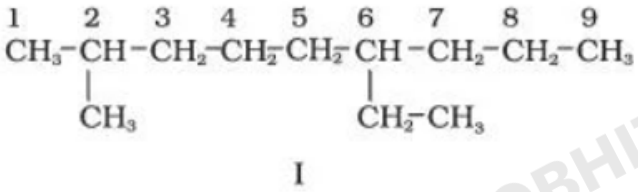
- **Abbreviations/Symbols**
  (i)Methyl = Me
  (ii) ethyl = Et
  (iii) propyl = Pr
  (iv) butyl = But

- **Branched alkyl structures**



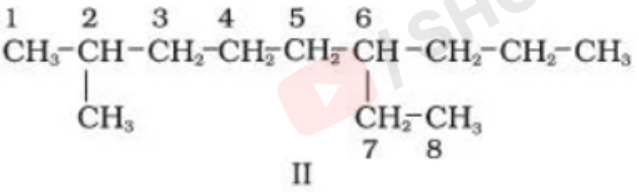
(c) Nomenclature of branched-chain alkanes:

1. Longest carbon chain in the molecule is identified
the longest chain is → parent or root chain



I

X Parent chain has 9 carbon atom



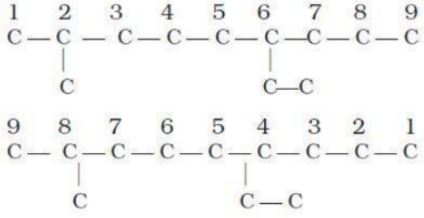
II

✓as parent has chain has only carbon
∴ not correct

(2.) Parent chains are numbered to identify the parent alkane and to locate the position of carbon atoms at which branching takes place due to the substitution of alkyl groups in place of hydrogen atoms.

- Numbering is done in such a way that the branched carbon atoms get the lowest possible numbers.

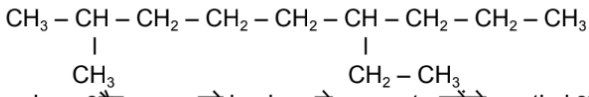
✓ As branched carbon is getting lowest no.



× as branched carbon is not getting lowest no.

3)

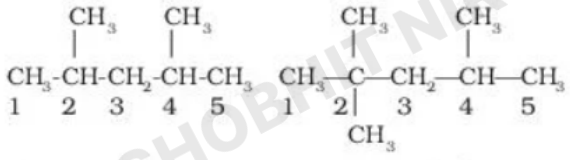
- The name of alkyl group is prefix to parent alkane
- position of substituents are given appropriate numbers.
- If different alkyl group present then list them in alphabetical order



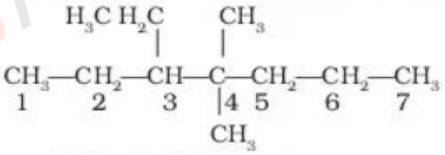
(numbers और group को hyphen से seperate करेंगे, methyl और nonane में gap नहीं होगा)

4)

- If 2 or more identical substituted the present numbers are separated by commas.
- Names of identical substituents are not repeated ; instead prefix di (for 2), tri(for 3), tetra(for 4), penta(for 5) are used.
- जब alphabetical order मेंनाम लिख रहेहैतो इन prefix को consider नहींकरेंगेl

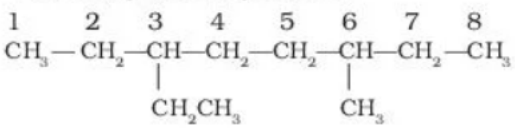


2,4-Dimethylpentane *2,2,4-Trimethylpentane*

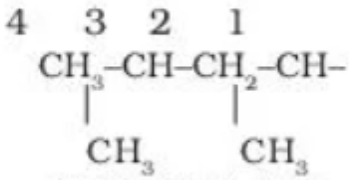


3-Ethyl-4,4-dimethylheptane

5. If 2 substituents are found in an equivalent position, the lower number is given to the one coming first in the alphabetical listing.



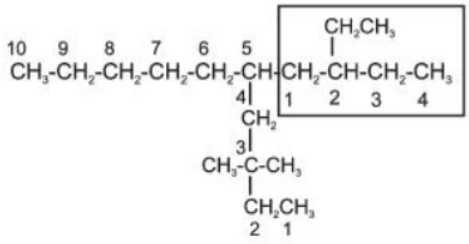
6.Carbon atom of the branch that attaches to the root alkane is numbered 1 as shown below



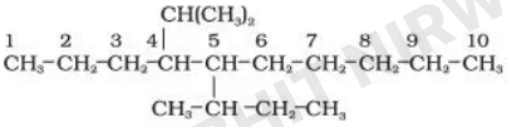
1,3-Dimethylbutyl-

7) In alphabetical order, the prefixes iso-and neo considered to be part of the fundamental name of alkyl group prefixes sec- and tert – are not part of the fundamental name.

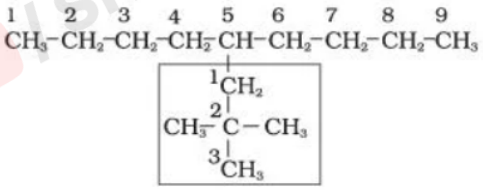
8)
- if 2 chains of equal size, then that chain is to be selected which contains
- After the selection of the chain, numbering is done from the end closer to the substitute.



5-(2-Ethylbutyl)-3,3-dimethyldecane
[and not 5-(2,2-Dimethylbutyl)-3-ethyldecane]



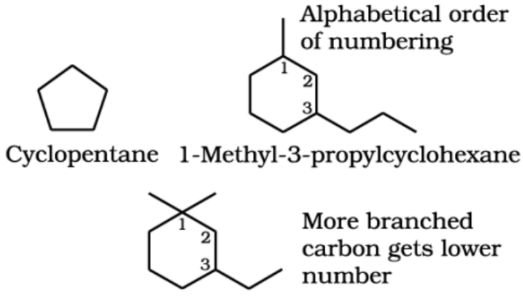
5-sec-Butyl-4-isopropyldecane



5-(2,2-Dimethylpropyl)nonane

d) Cyclic Compounds:

- A saturated monocylic compound is named by prefixing `cycle" to straight chain alkene.
- अगर side chain present हैतो जो branched chain alkanes के लिए rules है वही लगा दो l



Q8) Structures and IUPAC names of some hydrocarbons are given below. Explain why the names given in the parentheses are incorrect.

(a) $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - CH_3$

2, 5,6-Trimethyloctane (and not 3,4,7-Trimethyloctane)

(b) $CH_3 - CH_2 - \underset{\displaystyle CH_2CH_3}{\underset{|}{CH}} - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - CH_3$

3-Ethyl-5-methylheptane (and not 5-Ethyl-3-methylheptane)

Solution: (a) Lowest locant number 2,5,6 is lower than 3,5,7 (b) substituents are in equivalent position; lower number is given to the one that comes first in the name according to alphabetical order.

(iii) Nomenclature of organic compounds having functional group (s):

- Compounds having the same functional group undergo similar reactions.
- **Eg; CH3OH, CH3CH2OH and (CH3)2CHOH – all liberate hydrogen on reaction with sodium metal.**

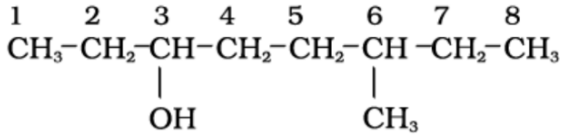
Table 12.4 Some Functional Groups and Classes of Organic Compounds

Class of compounds	Functional group structure	IUPAC group prefix	IUPAC group suffix	Example
Alkanes	-	-	-ane	Butane, $CH_3(CH_2)_2CH_3$
Alkenes	>C=C<	-	-ene	But-1-ene, $CH_2=CHCH_2CH_3$
Alkynes	-C≡C-	-	-yne	But-1-yne, $CH{\equiv}CCH_2CH_3$
Arenes	-	-	-	Benzene, 
Halides	-X (X=F,Cl,Br,I)	halo-	-	1-Bromobutane, $CH_3(CH_2)_2CH_2Br$
Alcohols	-OH	hydroxy-	-ol	Butan-2-ol, $CH_3CH_2CHOHCH_3$
Aldehydes	-CHO	formyl, or oxo	-al	Butanal, $CH_3(CH_2)_2CHO$
Ketones	>C=O	oxo-	-one	Butan-2-one, $CH_3CH_2COCH_3$
Nitriles	-C≡N	cyano	nitrile	Pentanenitrile, $CH_3CH_2CH_2CH_2CN$
Ethers	-R-O-R-	alkoxy-	-	Ethoxyethane, $CH_3CH_2OCH_2CH_3$
Carboxylic acids	-COOH	carboxy	-oic acid	Butanoic acid, $CH_3(CH_2)_2CO_2H$
Carboxylate ions	$-COO^-$	-	-oate	Sodium butanoate, $CH_3(CH_2)_2CO_2^-\ Na^+$
Esters	-COOR	alkoxycarbonyl	-oate	Methyl propanoate, $CH_3CH_2COOCH_3$
Acyl halides	-COX (X=F,Cl,Br,I)	halocarbonyl	-oyl halide	Butanoyl chloride, $CH_3(CH_2)_2COCl$
Amines	$-NH_2$, >NH,>N-	amino-	-amine	Butan-2-amine, $CH_3CHNH_2CH_2CH_3$
Amides	$-CONH_2$, -CONHR, $-CONR_2$	-carbamoyl	-amide	Butanamide, $CH_3(CH_2)_2CONH_2$
Nitro compounds	$-NO_2$	nitro	-	1-Nitrobutane, $CH_3(CH_2)_3NO_2$
Sulphonic acids	$-SO_3H$	sulpho	sulphonic acid	Methylsulphonic acid CH_3SO_3H

Rules

1. Identify the functional group, so that we can determine the appropriate suffix.
2. The longest chain of carbon atoms containing the functional group is numbered in such a way that the functional group is attached to the carbon atom possessing the lowest possible number in the chain.
3. In a polyfunctional compound, chose one functional group and the functional group is called as principle functional group. बाकी के functional group को appropriate prefixes से name करदो l
4. Priority of choosing function group in decreasing order. -COOH , - SO3H , -COOR (R =alkylgroup), COCl, -CONH2, -CN , -HC =O, >C=O, -OH,-NH2 , >C=C< , -C≡C-
5. –R, C6H5-, halogens (F, Cl, Br,I), -NO2, alkoxy (-OR), etc are always prefixed.Eg; hydroxyalkanone (compound मेंअगर और दोनो हैतो येनाम देंगे)HOCH2 (CH2)3CH2COCH3 → named as 7 hydoxyheptan-2-one ; not as z –oxoheptan-7-ol. BrCH2CH=CH2; named as 3 bromoprop-1-ene and not 1-Bromo- prop-2-ene.
6. **i)** If more than 1 functional group of the same type is present then their number is indicated by adding di, tri, etc and before the suffix
   ii) the full name of the parent alkane is written before the suffix.Eg: CH2(OH)CH2(OH) ; ethane -1,2-diol CH2 = CH-CH=CH2; buta -1,3-diene (अगर एक सेज्यादा double or triple bond present है तो ending –ne को निकल दो)

Q9)Write the IUPAC names of the compounds i-iv from their given structures.

(i) 

Solution:

• The functional group present is alcohol (OH). Hence the suffix is '-ol'.
• The longest chain containing -OH has eight carbon atoms. Hence the corresponding saturated hydrocarbon is octane.
• The -OH is on carbon atom 3. In addition, a methyl group is attached at 6th carbon.

Hence, the systematic name of this compound i**s 6-Methyloctan-3-ol.**

(ii) $\underset{6}{CH_3} - \underset{5}{CH_2} - \underset{4}{\overset{\overset{O}{||}}{C}} - \underset{3}{CH_2} - \underset{2}{\overset{\overset{O}{||}}{C}} - \underset{1}{CH_3}$

Solution:

The functional group present is ketone (>C=O), hence the suffix '-one'. The presence of two keto groups is indicated by 'di', hence suffix becomes 'dione'. The two keto groups are at carbons 2 and 4. The longest chain contains 6 carbon atoms, hence, the parent hydrocarbon is hexane. Thus, the systematic name is Hexane-2,4-dione.

(iii) $\underset{6}{CH_3} - \underset{5}{\overset{\overset{O}{||}}{C}} - \underset{4}{CH_2} - \underset{3}{CH_2} - \underset{2}{CH_2} - \underset{1}{COOH}$

Solution:

Here, two functional groups namely ketone and carboxylic acid are present. The principal functional group is the carboxylic acid group; hence the parent chain will be suffixed with 'oic' acid. The numbering of the chain starts from the carbon of the -COOH functional group. The keto group in the chain at carbon 5 is indicated by 'oxo'. The longest chain including the principal functional group has 6 carbon atoms; hence the parent hydrocarbon is hexane. The compound is, therefore, named as 5-Oxohexanoic acid.

(iv) $\underset{6}{\breve{C}H} \equiv \underset{5}{\breve{C}} - \underset{4}{\dot{C}H} = \underset{3}{\breve{C}H} - \underset{2}{\tilde{C}H} = \underset{1}{\dot{C}H_2}$

Solution:

The two C=C functional groups are present at carbon atoms 1 and 3, while the C≡C functional group is present at carbon 5. These groups are indicated by suffixes 'diene' and 'yne' respectively. The longest chain containing the functional groups has 6 carbon atoms; hence the parent hydrocarbon is hexane. The name of the compound, therefore, is Hexa-1,3-dien-5-yne.

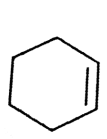
Q10)Derive the structure of (i) 2-Chlorohexane, (ii) Pent-4-en-2-ol, (iii) 3-Nitrocyclohexene, (iv) Cyclohex-2-en-1-ol, (v) 6-Hydroxy-heptanal.
Solution

Solution:

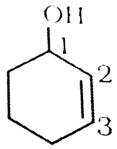
(i) 'hexane' indicates the presence of
6 carbon atoms in the chain. The functional group chloro is present at carbon 2. Hence, the structure of the compound is
CH3CH2CH2CH2CH(Cl)CH3

(ii) 'pent' indicates that parent hydrocarbon contains 5 carbon atoms in the chain. 'en' and 'ol' correspond to the functional groups C=C and -OH at carbon atoms 4 and 2 respectively. Thus, the structure is
CH2=CHCH2CH (OH)CH3

(iii) Six membered ring containing a carbon-carbon double bond is implied by cyclohexene, which is numbered as shown in (I). The prefix 3-nitro means that a nitro group is present on C-3. Thus, the complete structural formula of the compound is (II). The double bond is suffixed functional group whereas NO2 is prefixed functional group therefore double bond gets preference over –NO2 group:

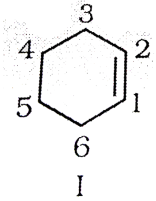


I

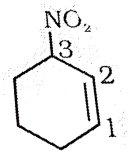


II

(iv) '1 – ol' means that the -OH group is present in C – 1. OH is suffixed functional group & gets preference over C=C.



I

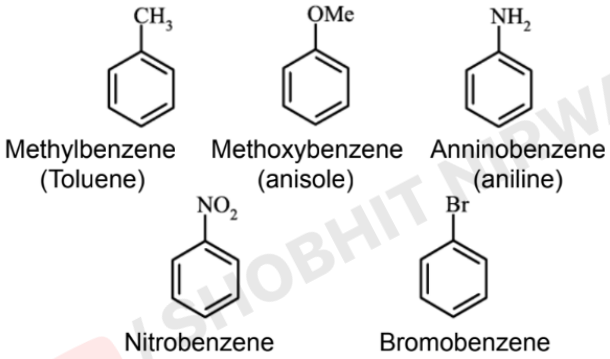


II

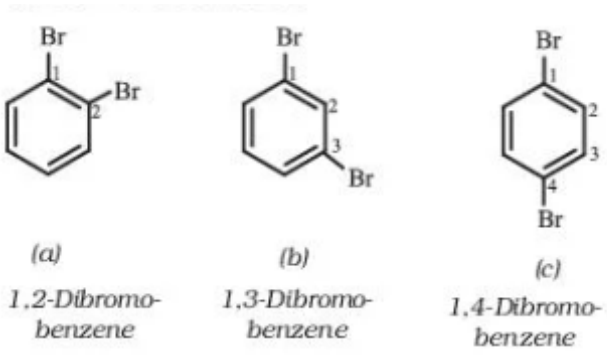
(v) ‘ heptanal’ indicated the compound to be an aldehyde containing seven carbon atoms in the parent chain. The ‘6 – hydroxy’ indicates the -OH group is present at carbon 6. **Thus, the structural formula of the compound is: CH3CH(OH)CH2CH2CH2CH2CHO. The carbon atom of -CHO of the group is included while numbering the carbon chain.**

(iv) Nomenclature of substituted benzene compounds:

1.) Substituent is placed as a prefix to word benzene.



2. If benzene ring is disubstituted, position of substitutions is defined by numbering the carbon atoms of ring such that the substituents are located at lowest numbers possible.

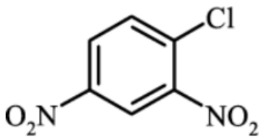


According to the above example
1,2- ortho (o) → ortho dibromobenzene
1,3 – meta(m)→ meta dibromobenzene
1,4 – para(p) → para dibromobenzene

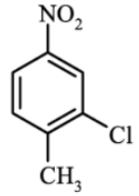
3. For tri or higher substituted benzene derivative , prefixes(o),(m) ,(p) cannot be used

∴ follow the lowest locant rule

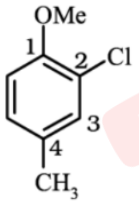
- Substituents of the base compound are given the number 1 and then the direction of numbering is chosen such that the next substituent gets the lowest number.
- Substituents should be in alphabet order.



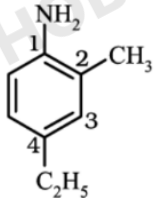
1- chloro -2,4- dinitrobenzene
(not 4-chloro,1,3 – dinitrobenzene)



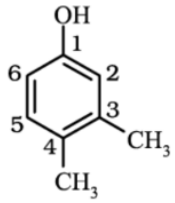
2-chloro -1-methyl-4-nitrobenzene
(not 4-methyl-5-chloro-nitrobenzene)



2 – Chloro – 4 - methylanisole



4-ethyl-2-methylaniline



3,4 -dimethylphenol

Important points:

- जब benzene ring functional group सेattached होता हैतो उसेहम as a substituents consider करतेहैं, instead as parent.
- Benzene as substituent is phenyl(ph)

Q11)Write the structural formula of:

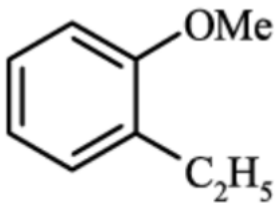
(a) o-Ethylanisole,

(b) p-Nitroaniline,

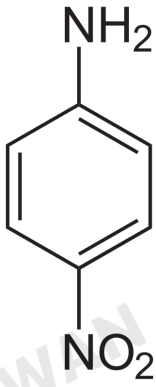
(c) 2,3 - Dibromo -1 - phenylpentane,

(d) 4-Ethyl-1-fluoro-2-nitrobenzene.

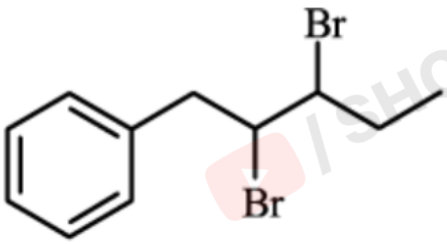
a)



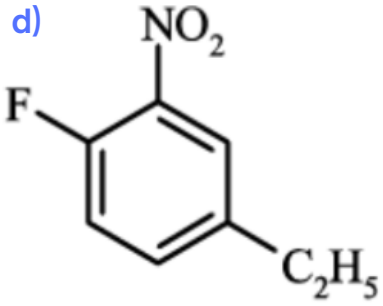
b)



c)

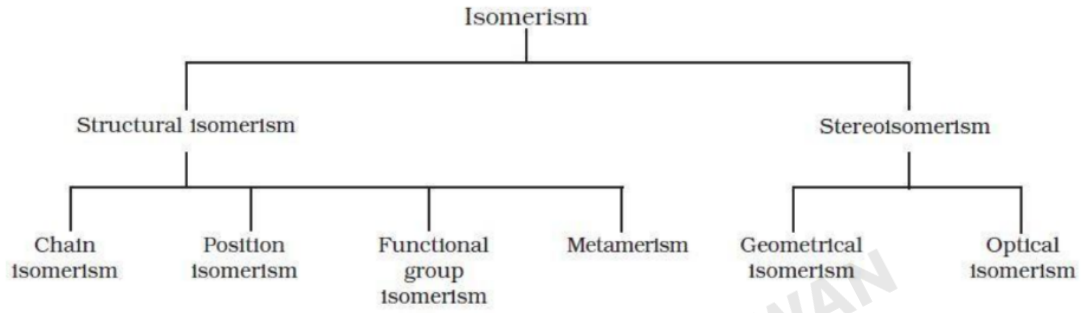


d)



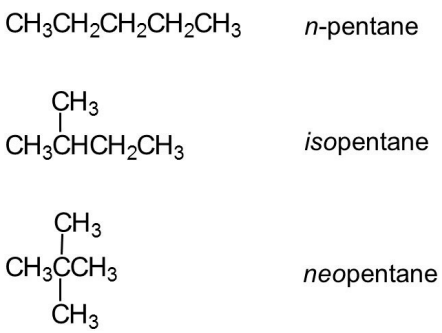
Isomerism

Definition: The phenomenon of the existence of 2 or more compounds possessing the same molecular formula but different properties such compounds are called isomers.



(i) Structural Isomerism:
Have some molecular formula but different structures(manners in which atoms are linked)

- **Chain isomerism:** 2 or more compounds have a similar molecular formula but different carbon skeletons are chain isomers and the phenomenon is termed as chain isomerism.

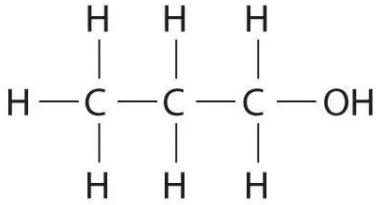


→ parent chain or carbon skeleton differ करेगी l

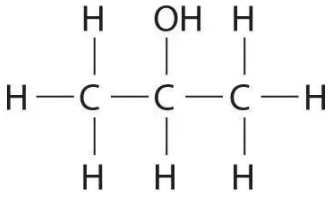
- **Position isomerism:** 2 or more compounds differ in the position of substituent Atom or functional group on the carbon skeleton.

→carbon skeleton or parent chain same रहेगी बस substituted atom or functional group की position change होगी l

Eg: position isomers of C3H8O



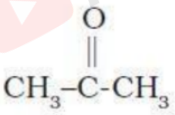
1-Propanol (*n*-propanol)



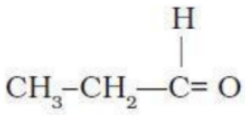
2-Propanol (isopropanol)

- **Functional group isomerism:** 2 or more compounds having the same molecular formula but different functional groups are called functional isomers and this phenomenon is called functional group isomerism

Eg: C3H6O aldehyde भी represent करता हैऔर ketone भी!



Propanone



Propanal

- **Metamerism:** arises due to different alkyl chains on either side of the functional group in the molecule.
  मतलब functional group के अगल बगल जो chains होंगेवो differ करेंगेl

(ii) Stereoisomerism:

Definition: compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space. मतलब bonds और उनका sequence same होगा पार atoms or groups की position 3 – D space में differ करेगी l

FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM:

- In the organic reaction: organic molecule (substance) reacts with an attacking reagent and leads to the formation of one or more intermediate(s) and finally products(s)
- **Substrate:** supplies carbon to the new bond
- **Reagent:** other reactant
- अगर दोनो reactants carbon supply कर रहेहैतो किसी एक को substrate मान लो In this case दो carbon के बीच का covalent bond या carbon & other atom के बीच का bond break hota और नया bond बंता हैl

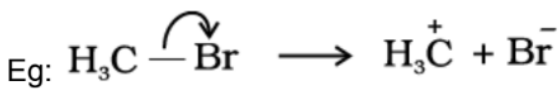
→ **Reaction Mechanism:** A sequential account of each step describing details of electron movement, energetics during bond cleavage & bond formation & the rates of transformation of reactants into products (kinetics)
[ncert के boldLines]

- Reaction mechanism हमे compounds की reactivity समझने में help करता हैऔर organic compounds के synthesis को plan करनेमेंhelp करता हैl

(i) Fission Of a Covalent Bond: Fission → bond ka break होना
Covalent bond 2 तारीके से break होता हैं→
1. Homolytic Cleavage
2. Heterolytic Cleavage

1. Heterolytic Cleavage:

- Bond breaks in such a way that the shared pair of electrons remains with one of the fragments.
- Heterolysis के बाद एक atom का sextet electronic configuration(valence electron 6 होतेहैं) और positive charge और एक दसरू atom का valence octet with at least one lone pair और negative charge.

Eg: 

Carbocation:

species having carbon atoms possessing a sextet of (carbonium ion) electrons & a positive charge.

Primary Carbocation	**One carbon attached directly to carbocation**	**CH3CH2 (ethyl cation)**
Secondary carbocation	**2 carbons attached directly to carbocation**	**(CH3)2CH (isopropyl cation)**
Tertiary Carbocation	**3 carbons attached directly to carbocation**	**(CH3)3+C (tert–butyl cation)**

- **Carbocations are highly unstable & reactive species.**

Stability order: +CH3 < CH3+CH2 < (CH3)2+CH < (CH3)3+C

- Has a trigonal planar shape with positively charged carbon which is sp2 hybridized.
- 3 hybridized C (sp2) hybridized orbitals, 1s orbital of each 3 hydrogen atoms, remaining carbon orbital is perpendicular to the molecular plan & contains no electrons.

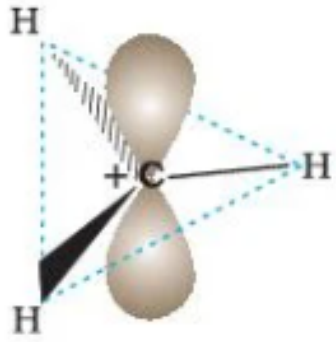


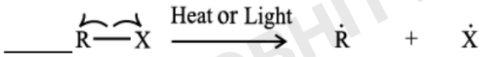
Fig. 12.3(a) *Shape of methyl carbocation*

Carbanion: carbon gets the shared pair of electrons & carries a negative charge,

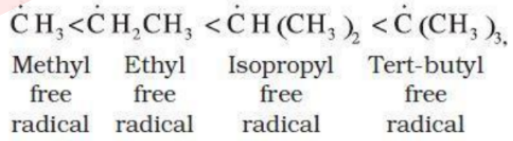
Carbanions are also unstable & reactive species.
→ Heteropolar or ionic or polar reactions: reactions that proceed through heterolytic bond cleavage.

2. Homolytic fission

- One of the electrons of the shared pair in a covalent bond goes with each of bonded atoms.
- Single electron movement is shown by a 'half–headed' (fish hook) curved arrow.
- **Free Radicals → neutral species which contains an unpaired electron.**



- Radicals are also very reactive.
- Classified as primary, secondary or tertiary



- **Free radical/homopolar/non–polar →** reactions which proceed by homolytic fission.

Nucleophiles and Electrophiles

Nucleophile:- reagent that brings an electron i.e nucleus seeking & the reaction Is called nucleophile.
Electrophile:- reagent that takes away an electron pair i.e electron seeking and the reaction is called electrophilic.

- Polar reaction के time nucleophile substrate के उस electrophilic center पे attack करता है जो atom or part of electrophile electron deficient हैI ईसी तरह electrophile substrate के उस nucleophilic centre पे attack करता हैजो electron rich centre है

∴ Electrophiles receive electron pairs from nucleophiles when 2 undergo bonding interaction.

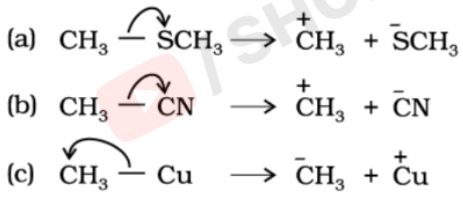
- **Examples of Nucleophile →** negatively charged ions with lone pairs of the electron [hydroxide (HO-), cyanide(NC-) & carbanions (R3C:)]
  Neutral molecules [H2O: , R3 N: , R2NH]

- **Examples of electrophiles →** carbocations (CH3), neutral molecules having functional groups [carbonyl group(>C=O) or alkyl halide (R3C-X, X is halogen)]

- **Alkyl halide acts as electrophiles due to polarity of the C – X bond partial positive charge is generated on carbon atoms.**

Q12)Using curved-arrow notation, show the formation of reactive intermediates when the following covalent bonds undergo heterolytic cleavage.
(a) CH3–SCH3
(b) CH3–CN
(c) CH3–Cu

Solution



Q13) Giving justification, categorise the following molecules/ions as a nucleophile or electrophile:

$$HS^-, BF_3, C_2H_5O^-, (CH_3)_3N:,$$

Solution:
Nucleophiles: These species have unshared pair of electrons, which can be donated & shared with an electrophile.

$$HS^-, C_2H_5O^-, (CH_3)_3N:, H_2N:^-$$

Electrophiles: Reactive sites have only six valence electrons; can accept electron pair from a nucleophile.

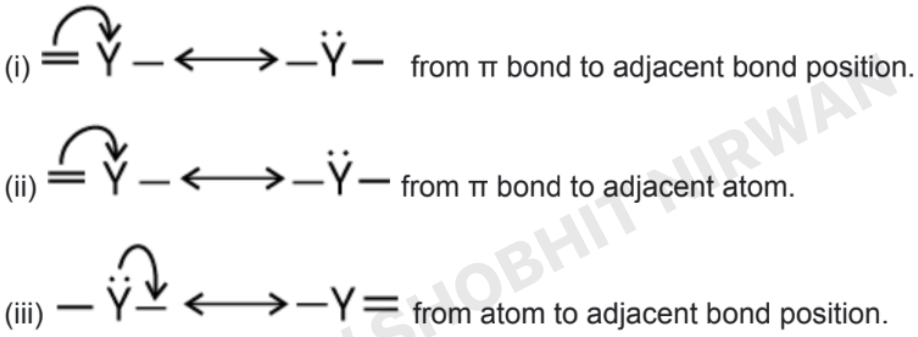
$$BF_3, \overset{+}{C}H_3, -\overset{+}{C}=O, \overset{+}{N}O_2$$

Q14) Identify the electrophilic centre in the following: CH3CH=O, CH3CN, CH3I.

Solution:
Among CH3HC*=O, H3CC*≡N, and
H3C*–I, the starred carbon atoms are electrophilic centers as they will have a partial positive charge due to the polarity of the bond.

Electron Movement in Organic Reactions:

- Movement of electron can be shown by curved arrow.

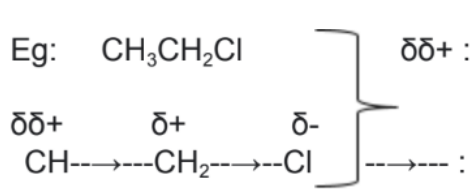


(iv) Electron Displacement Effects in covalent bonds:

- Electron displacement may take place due to atom or a substituent group or in the presence of an attacking reagent.
- Electron displacement due to the influence of atom or substituent group present in the molecule cause permanent polarisation of bond, eg: Inductive Effect and resonance
- Electron displacement due to Attacking Reagent cause temporary electron displacement called as electromeric effect or polarizability effect.

(v) Inductive Effect:

- जब दो atoms (जिनकी electronegativity differ करती हो) के बीच covalent bond बंता है तो atom की electron density ज़्यादा electronegative की तरफ होती हैl और इस polarity shift के वजह सेpolar covalent bond बनता हैl



→ **Definition:** polarisation of σ bond caused by polarisation of adjacent σ bond.

- Decreases rapidly as not of intervening bonds increase (or as distance increase)और गायब हो जाता है 3rd bond आनेतक

- Substituent atom can be electron – withdrawing group (जो e- को अपने तारफ खीचेगा) or electron -donation (जो e- को देगा)

- e- withdrawing → halogens, nitro(-NO2), cyano(-CN), carboxy(-COOH), ester(-COOR), aryloxy(-OAr, eg:- OC6H5)

- e- donating → (-CH3), ethyl (-CH2-CH3)

Q15)Which bond is more polar in the following pairs of molecules:
(a) H3C-H, H3C-Br
(b) H3C-NH2H3C-OH
(c) H3C-OH, H3C-SH

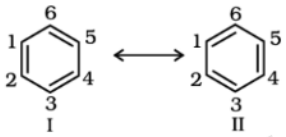
Solution:
(a) C–Br, since Br is more electronegative than H, (b) C–O, (c) C–O

Q16)In which C–C bond of CH3CH2CH2Br, the inductive effect is expected to be the least?

Solution:
The magnitude of the inductive effect diminishes as the number of intervening bonds increases. Hence, the effect is least in the bond between carbon-3 and hydrogen.

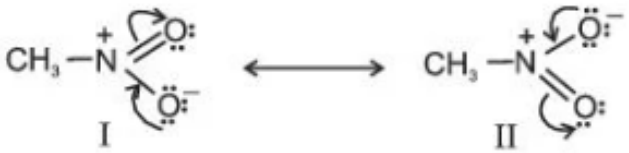
(vi) Resonance Structure

- As benzene के पास alternate double और single bond है cyclic structure में तो benzene के दो bond lengths होनेचाहिए, पर experimentally benzene has only one bond length.
- We cannot represent benzene by a single structure.



}सही तरिका benzene को represent करने का ये है।

- The Resonance structures (canonical structures or contributing structures) are hypothetical and individually do not represent any real molecule **[ncert bold lines]**
- 2 N – O bonds of nitromethane are of the same length (intermediate between a N– O single bond and a N=O double bond). The actual structure of nitromethane is therefore a resonance hybrid of the 2 canonical forms I and II



- The energy of actual structure < energy of any conical structure (resonance hybrid)
- Resonance stabilization energy → energy difference between actual Or resonance energy structure and lowest energy resonance.
- More the resonating structure, more the resonance energy.

Rules for writing Resonating structures:

Resonance structure have:

- the same positions of nuclei
- the same number of unpaired electrons.

Q17) Which resonating structure is most stable ?

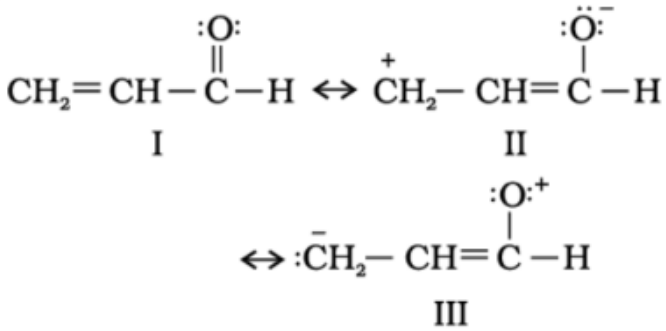
Solution:

1. One which has more covalent bonds.
2. all atoms with an octet of electrons (except hydrogen which have a duplet)
3. less separation of opposite charges.
4. -ve charge on the electronegative atom & +ve charge on the electropositive atom.
5. more dispersal of charge, is more stable than others.

Q18) Write resonance structures of CH3COO– and show the movement of electrons by curved arrows.

Solution: First, write the structure and put unshared pairs of valence electrons on appropriate atoms. Then draw the arrows one at a time moving the electrons to get the other structures.

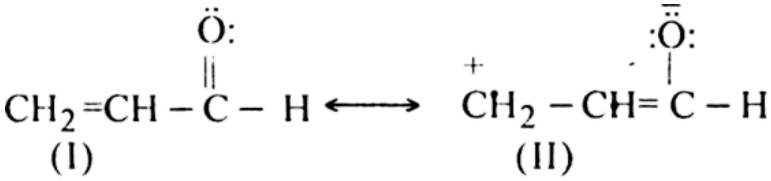
Stability: I > II > III



I II III

Q19)Write resonance structures of CH2=CH–CHO. Indicate the relative stability of the contributing structures.

Solution: Most stable, more number of covalent bonds, each carbon, and the oxygen atom has an octet and no separation of opposite charge II: negative charge on more electronegative atom and positive charge on more electropositive atom; III: does not contribute as oxygen has a positive charge and carbon has a negative charge, hence least stable].



Q20)Explain why the following two structures, I and II cannot be the major contributors to the real structure of CH3COOCH3.

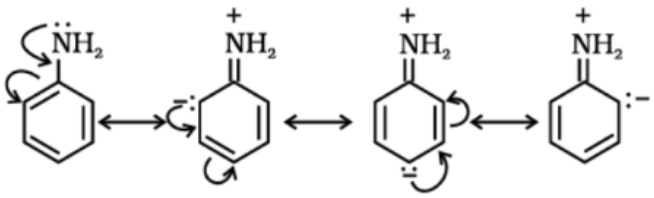
Solution: The two structures are less important contributors as they involve charge separation. Additionally, structure I contain a carbon atom with an incomplete octet.

(vii) Resonance Effect:

Definition: Polarity produced in the molecule by the interaction of z π bonds or between a π bond and lone pair of electrons present on an adjacent atom.

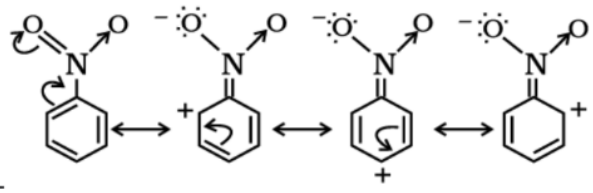
(a) Positive Resonance Effect (+R effect):

- Transfer of e- away from an atom or substituent group attached to conjugated system.
- Halogen, -OH, -OR, -OCOR, -NH2, -NHR, -NR2, -NHCOR



(b) Negative Resonance Effect (-R effect):

- Transfer of electrons towards the atoms or substituent group attached to the conjugated system.
- -COOH, -CHO, >C=O, -CN, -NO2



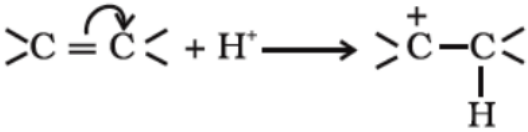
→ **Conjugate system:** Presence of alternate single and double bonds in an open chain or cyclic system.

(viii) Electromeric Effect:

- Is a temporary effect.
- Organic compounds having a multiple bond (double or triple bond) show this effect in the presence of an attacking reagent only.
- Complete transfer of a shared pair of π – electrons to one of the atoms joined by a multiple bond an the demand of an attacking reagent.

(a) Positive Electromeric Effect (+E effect):

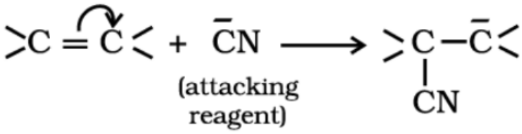
- π electrons of multiple bonds are transferred to that atom to which the reagent gets attacked.



Positive Electromeric Effect

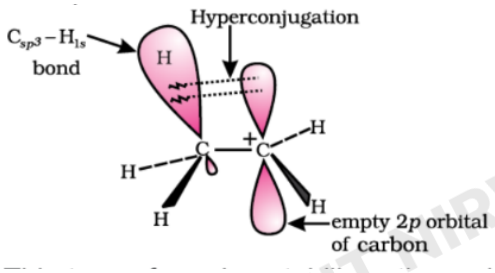
(b) Negative Electromeric Effect (-E effect):

- π electrons of the multiple bonds are transferred to that atom to which the attacking reagent does not get attacked.

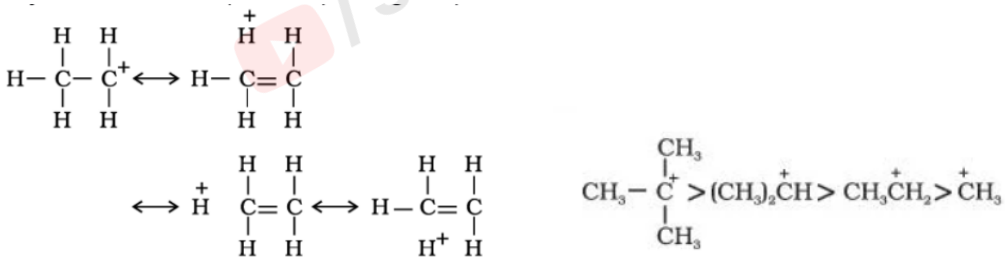


(ix) Hyperconjugation:

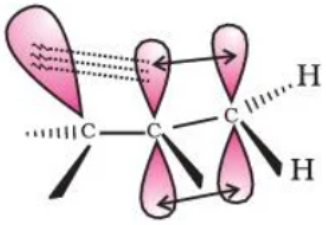
- Alkyl group के C – H bond के σ e - का delocalise होना unsaturated system के atom या unshared p orbital के atom की तरफ l और इनके बीच partial conjugation भी develop होता हैl
- Involves delocalization of σ e- of the C – H bond of an alkyl group directly attached to an atom of an unsaturated system or to an atom with an unshared p orbital.
- σ e- of C – H bond of the alkyl group entire into partial conjugation with the attached unsaturated system or with unshared p orbital.
- Is as permanent effect.

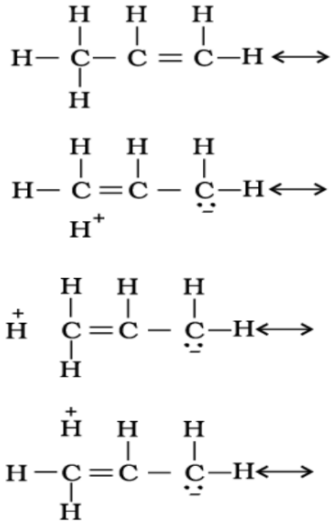


- This type of overlap stabilizes the carbocation because electron density from the adjacent σ bond helps in dispersing the positive charge



- **Hyperconjugation is also possible in alkenes & alkylarenes.**





Q21) Explain why (CH3)3C+ is more stable than CH3CH2 & CH3 has nine C-H bonds.

Solution: In C+H3, vacant p orbital is perpendicular to the plane in which C –H bonds lie; hence cannot overlap with it. Thus, C+H3 lacks hyperconjugative stability..

(x) Types of organic reactions and mechanisms

(a) Substitution reactions.
(b) Addition reactions.
(c) Elimination reactions.
(d) Rearrangement reactions.

METHODS OF PURIFICATION OF ORGANIC COMPOUNDS:

- Organic compound को extract करनेके बाद उन्हे purify करना जरूरी हैl
- Purity of compound हम compound के melting और boiling point से check करते हैंl
- Pure compounds have sharp melting and boiling points.

→ Chromatographic & Spectrographic:

(i) Sublimation:

- On heating some solid to vapor state without passing through the liquid state.
- Use to separate sublimable compounds from non – sublimable impurities.

(ii) Crystallisation:

- Used for purification of solid organic compounds.
- Based on the difference in solubilities of compound and impurities in a suitable solvent.
- Impure compound को ऐसे solvent में dissolve करो जिसमेवो sparingly soluble हो room temperature पेऔर अच्छे से soluble हो high temperature.
- और अब solution को ठंडा करनेपर pure compound crystalise हो जाता हैऔर हम उसे filtre करके निकल देतेहैं l
- The filtrate (mother liquor) contains impurities and a small quantity of the compound.

- Impurities that impart colour to the solution are removed by adsorbing over activated charcoal.
- Repeated crystallization is necessary for the purification of compounds containing impurities of comparable solubilities.

(iii) Distillation:

- Used to separate volatile liquids from non–volatile impurities & the liquids having a sufficient difference in their boiling points.
- Liquids having different boiling points evaporate at different temperatures vapours are cooled & the liquid so formed is collected separately.
- Chloroform & aniline are separated by distillation.
- The liquid mixture is taken & heated carefully, on boiling component are formed first.
- Vapours are condensed by using a condenser & liquid is collected in a receiver.
- The vapours of the higher boiling component form later and the liquid can be collected separately.

(a) Fractional Distillation:

- अगर दोनो liquid के boiling points मेंज्यादा difference नहीं हैतो हम simple distillation वाला method नहीं use कर सकतेl
- Vapours of liquid are formed within the same temperature range and are condensed simultaneously.
- ऐसे cases में fractional distillation की technique use करतेहैंl
- In this technique vapours of the liquid mixture are passed through a fractionating column before condensation.
- Vapours of liquid with a higher boiling point condense before the vapours of the liquid with a lower boiling point.
- Vapours rising up in the fractionating column become richer in more volatile components.

- Fractionating column provides surface for heat exchange for heat exchange between ascending vapours descending condensed liquid.
- Some of the condensing liquid in the fractionating column obtains heat from the ascending vapours and vaporizers and the vapours become richer in low boiling component.
- Vapours of low boiling component ascend to top of column and on reaching the top vapours become pure in low boiling component & pass through condenser & the pure liquid is collected in receiver.
- After a series of successive distillations, the remaining liquid in the distillation flask gets enriched in the high boiling component.
- Theoretical Plate – each successive condensation & vapourisation unit in the fractionating column.
- This technique is used in the crude oil petroleum industry

(b) Distillation under the Reduced Pressure:

- Used to purify liquids having very high boiling points & these which decompose at or below their boiling points.
- Such liquids are made to boil at a temperature lower than their normal boiling points by reducing the pressure on their surface.
- The pressure is reduced with the help of a water pump or vacuum pump.
- Glycerol can be separated from spent – lye in the soap industry by using this technique.

(c) Steam Distillation:

- Applied to separate substances which are steam volatile and are immiscible with water.
- Steam from a steam generator is passed through a heated flask containing the liquid to be distilled.
- A mixture of steam & the volatile organic compound is condensed & collected.
- The compound is later separated from water using a separating funnel.
- The liquid boils when the sum of vapour pressure due to the organic liquid (p1) and that due to water (p2) becomes equal to the atmospheric pressure (p) i.e $p = p1 + p2$.

- p1 is lower than p, the organic liquid vaporizes at a lower temperature than its boiling point.
- If one of the substances in the mixture is water and the other, a water-insoluble substance, then the mixture will boil close to but below, 373K
- A mixture of water and substance is obtained which can be separated by using a separating funnel.
- Aniline is separated by this technique from an aniline water mixture

(iv) Differential extraction:

- When the organic compound is present in an aqueous medium, it is separated by shaking it with an organic solvent in which it is more soluble than in water.
- Organic solvent and aqueous solution should be immiscible with each other so that they form two distinct layers which can be separated by the separatory funnel
- The organic solvent is later removed by distillation or by evaporation to get back the compound.
- Differential extraction is carried out in a separatory funnel.
- If the organic compound is less soluble in the organic solvent, a very large quantity of solvent will be required to extract even a very small quantity of the compound.
- The technique of continuous extraction is employed in such cases.
- In this technique, the same solvent is repeatedly used for the extraction of the compound.

(V) Chromatography:

- Technique extensively used to separate mixtures into their components and also to test the purity of compounds.
- Chroma - means color, as before this method was used to separate colourfulsubstances found in the plants.
- Mixture of substances is applied onto the stationary phase, which may be solid or liquid.
- A pure solvent, a mixture of solvents or gas is allowed to move slowly over the stationary phase.
- Components of the mixture get gradually separated from one another and the moving phase is called as mobile phase.
- Chromatography is classified into

a) Adsorption Chromatography:

- Based on the fact that different compounds are adsorbed on an adsorbent to different degrees.
- Commonly used adsorbents - silica gel and alumina.

-> **Based on differential adsorption there are two types of chromatographic techniques.**

b) Column Chromatography:

- Involves separation of a mixture over a column of absorbent (stationary phase) packed in a glass tube.
- Mixture adsorbed on adsorbent is placed on the top of the adsorbent column packed in a glass tube.
- An appropriate eluate (elution -extracting one material from another by washing with a solvent) which is a liquid or mixture of liquids is allowed to flow down thecolumn slowly .
- Depending upon degree the degree to which the compounds are adsorbed, complete separation takes place.
- Most readily adsorbed substances are retained near the top end others come down to various distance in the column

c) Thin layer chromatography:

- Involves the separation of substances of a mixture over a thin layer of adsorbent coated on a glass plate.
- The plate is known as a chrome plate or thin-layer chromatography plate(TLC)
- The solution of the mixture to be separated is applied as a small spot about 2cm above one end of the TLC plate.
- The glass plate is then placed in a closed jar containing the eluant.
- Mixtures move up along with eluent depending on their degree of adsorption and separation takes place.
- Retardation factor (Rf value) - relative adsorption of each component of the mixture.

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

- spots of coloured compounds are visible on TLC plates due to their original colour.
- spots of colourless compounds which are invisible to the eye but fluoresce can be detected by putting the plate under ultra ultraviolet light.
- Another detection technique is to place the plate in a covered jar containing a few crystals of iodine.
- Spots of compounds, which adsorb iodine, will show up as brown spots.
- Sometimes an appropriate reagent may also be sprayed on the plate. For example, amino acids may be detected by spraying the plate with a ninhydrin solution.

d) Partition chromatography:

- Is based on the continuous differential partitioning of components of a mixture between stationary and mobile phases.
- Paper chromatography is a type of partition chromatography, a special quality paper known as chromatography paper is used.
- Chromatography paper contains water trapped in it, which acts as the stationary phase.
- A strip of chromatography paper spotted at the base with the solution of the mixture is suspended in a suitable solvent or a mixture of solvents. This solvent acts as the mobile phase.
- The solvent rises up the paper by capillary action and flows over the spot.The paper selectively retains (continue to have) different components according to their differing partition in the two phases. 6
- The paper strip so developed is known as a chromatogram.
- The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram.
- The spots of the separated colourless compounds may be observed either under ultraviolet light or by the use of an appropriate spray reagent as discussed under thin layer chromatography.

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

→ इसमे हम यह पढेंगेकी हम कीसि भी compound को केसे detect करे कीसि भी organic compound मे |

i) Detection of Carbon and Hydrogen

- Carbon और hydrogen को हम copper(II) oxide के साथ heat करके detect करते हैं|
- Carbon present in the compound is oxidised to carbon dioxide carbon(tested with lime water which develops turbidity) and hydrogen to water (tested with anhydrous copper sulphate which turns blue)

$$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$$

$$2H + CuO \xrightarrow{\Delta} Cu + H_2O$$

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + H_2O$$

$$5H_2O + CuSO_4 \longrightarrow \underset{\text{White}}{CuSO_4.5H_2O}$$
Blue

ii) Detection of Other elements

- **Lassaigne's test -** nitrogen, sulfur, halogens, and phosphorus present in the organic compounds are detected by this test
- Elements ate converted from covalent form to ionic form by fusing compound with sodium metal.

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$Na + X \xrightarrow{\Delta} Na\,X$$
(X = Cl, Br or I)

C, N, S, and X come from organic compounds.

Cyanide, sulfide, and halide of sodium so formed on sodium fusion are extracted from the fused mass by boiling it with distilled water. This extract is known as sodium fusion extract. Sodium fusion extract - extract formed when cyanide, sulfide and halide of sodium formed on sodium fusion are extracted from the fused mass by boiling it with distilled water

(a) Test for Nitrogen:

- पहलेहम sodium fusion extract को iron(ll) sulphate के साथ boil करेंगेऔर फिर उसके बाद sulphuric acid के साथ acidify करेंगे।
- prussian blue colour का formation nitrogen के presence का indication है।
- sodium cyanide पहले iron(ll) sulphate के साथ react करके sodium hexacyanoferrate(ll) बनाता है।
- अब concentrated sulphuric acid के साथ heat करनेपर थोड़ेiron(ll) के ions iron(lll) मे हो जाते है जो sodium hexacyanoferrate(ll) के साथ react करते है iron (lll) hexacyanoferrate (ll) बनानेके लिए जोकि prussian blue colour का होता है।

$$6CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3.xH_2O}$$

(b) Test of Sulphur:

- Sodium fusion extract को acetic acid के साथ acidify करनेपर और lead sulphide add करनेपर एक black precipitate बनता हैजो sulphur के presence का indication है। S2− + Pb2+ → PbS
- Sodium fusion extract को sodium nitroprusside के साथ react करनेपर violet colour नजर आता हैजो sulphur के presence का indication है।

$$S^{2-} + [Fe(CN)_5NO]^{2-} \longrightarrow \underset{\text{Violet}}{[Fe(CN)_5NOS]^{4-}}$$

- अगर organic compound मे nitrogen और sulphur दोनो present है तो sodium thiocyanate बनता है। येreaction blood red colour देता है and no Prussian blue as there are no free cyanide ions.

$$Na + C + N + S \longrightarrow NaSCN$$

$$Fe^{3+} + SCN^- \longrightarrow \underset{\text{Blood red}}{[Fe(SCN)]^{2+}}$$

- If sodium fusion is carried out with excess sodium, the thiocyanate decomposes to yield cyanide and sulfide. These ions give their usual tests.

$$NaSCN + 2Na \longrightarrow NaCN + Na_2S$$

(c) Test for halogens:

- Sodium fusion extract is acidified with nitric acid and then treated with silver nitrate.
- The white precipitate, soluble in ammonium hydroxide shows the presence of chlorine.
- A yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine and a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.

$$X^- + Ag^+ \longrightarrow AgX$$

X represents a halogen – Cl, Br or I.

- If nitrogen or sulfur is also present in the compound, the sodium fusion extract is first boiled with concentrated nitric acid to decompose cyanide or sulfide of sodium formed during Lassaigne's test.
- These ions would otherwise interfere with the silver nitrate test for halogen

(d) Test for Phosphorus:

- The compound is heated with an oxidizing agent (sodium peroxide).
- The phosphorus present in the compound is oxidized to phosphate.
- The solution is boiled with nitric acid and then treated with ammonium molybdate.
- A yellow coloration or precipitate indicates the presence of phosphorus.

$$Na_3PO_4 + 3HNO_3 \rightarrow H_3PO_4 + 3NaNO_3$$

$$\underset{\text{Ammonium molybdate}}{H_3PO_4 + 12(NH_4)_2MoO_4} + 21HNO_3 \rightarrow \underset{\text{Ammonium phosphomolybdate}}{(NH_4)_3PO_4.12MoO_3} + 21NH_4NO_3 + 12H_2O$$

QUANTITATIVE ANALYSIS:

- Helps chemists in the determination of mass percent of elements present in a compound.
- Required for the determination of empirical and molecular formulas. The percentage composition of elements present in an organic compound is determined by the following methods:

i) Carbon and Hydrogen

- Known mass of an organic compound is burnt in the presence of excess of oxygen and copper(II) oxide
- Carbon and hydrogen in the compound are oxidised to carbon dioxide and water respectively.

$$C_xH_y + (x + y/4)\,O_2 \longrightarrow x\,CO_2 + (y/2)\,H_2O$$

- The mass of water produced is determined by passing the mixture through a weighed U-tube containing anhydrous calcium chloride.
- Carbon dioxide is absorbed in another U-tube containing a concentrated potassium hydroxide solution. (tubes are connected in series)
- The increase in masses of calcium chloride and potassium hydroxide gives the amounts of water and carbon dioxide from which the percentages of carbon and hydrogen are calculated.

- **Let the mass of the organic compound be m g,**
- mass of water and carbon dioxide produced by m1 and m2 g respectively;
- Percentage of carbon= 12 × m2 × 100/44 × m
- Percentage of hydrogen = 2 × m2 × 100/18 × m

Q22) On complete combustion, 0.246 g of an organic compound gave 0.198g of carbon dioxide and 0.1014g of water. Determine the percentage composition of carbon and hydrogen in the compound.

Solution:

Percentage of carbon = 12 x 0.198 x 100 /44 x 0.246 = 21.95%

Percentage of hydrogen = 2 x 0.1014 x 100 /18 x 0.246 = 4.58%

ii) Nitrogen

There are two methods for the estimation of nitrogen: **(a) Dumas method and (b) Kjeldahl's method.**

(a) Dumas method:

- The nitrogen-containing organic compound, when heated with copper oxide in an atmosphere of carbon dioxide yields free nitrogen in addition to carbon dioxide and water.

$$C_x H_y N_z + (2x + y/2)\, CuO \rightarrow x\, CO_2 + y/2\, H_2O + z/2N_2 + (2x + y/2)\, Cu$$

- Traces of nitrogen oxides formed, if any, are reduced to nitrogen by passing the gaseous mixture over a heated copper gauze.
- The mixture of gases so produced is collected over an aqueous solution of potassium hydroxide which absorbs carbon dioxide.
- Nitrogen is collected in the upper part of the graduated tube .

- **Let the mass of organic compound = m g**
- **The volume of nitrogen collected = V1 mL**
- **Room temperature = T1K**
- **Volume of nitrogen at STP=P1 V1X 273/ 760 X T1 (Let it be V mL)**

Where p1 and V1 are the pressure and volume of nitrogen, p1 is different from the atmospheric pressure at which nitrogen gas is collected. The value of p1 is obtained

by the relation;

P1 = Atmospheric pressure – Aqueous tension 22400 mL N2 at STP weighs 28g

V mL N2 at STP weighs=28×V/22400g

Percentage of nitrogen = 28×V×100/22400×m

Q23) In Dumas' method for estimation of nitrogen, 0.3g of an organic compound gives 50mL of nitrogen collected at 300K temperature and 715mm pressure. Calculate the percentage composition of nitrogen in the compound. (Aqueous tension at 300K=15 mm)

Solution:

The volume of nitrogen collected at 300K and 715mm pressure is 50 mL

Actual pressure = 715-15 =700 mm

The volume of nitrogen at STP=273×700×50/300×760 = 41.9mL

- 22,400 mL of N2 at STP weighs = 28 g
- 41.9 mL of nitrogen weighs = 28×41.9/22400g

Percentage of nitrogen = 28×41.9×100/22400×0.3 =17.46 %

(b) Kjeldahl's method:

- The compound containing nitrogen is heated with concentrated sulphuric acid.
- Nitrogen in the compound gets converted to ammonium sulphate.
- The resulting acid mixture is then heated with excess of sodium hydroxide.
- The liberated ammonia gas is absorbed in an excess of standard solution of sulphuric acid.
- The amount of ammonia produced is determined by estimating the amount of sulphuric acid consumed in the reaction.

- It is done by estimating unreacted sulphuric acid left after the absorption of ammonia by titrating it with a standard alkali solution. The difference between the initial amount of acid taken and that left after the reaction gives the amount of acid reacted with ammonia.

$$\text{Organic compound} + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 \xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

- **Let the mass of organic compound taken = m g**
- **Volume of H2SO4 of molarity, M, taken = V mL**
- **The volume of NaOH of molarity, M, used for titration of excess of H2SO4 = V1mL**
- **V1mL of NaOH of molarity M = V1/2 mL of H2SO4 of molarity M**
- **Volume of H2SO4 of molarity M unused = (V – V1/2) mL**
- **(V- V1/2) mL of H2SO4 of molarity M = 2(V-V1/2) mL of NH3 solution of molarity M.**
- **1000 mL of 1 M NH3 solution contains 17g NH3 or 14 g of N**
- **2(V-V1/2) mL of NH3 solution of molarity M contains:**
- **14 X M X 2(V – V1/2)/1000 gN**

Percentage of N= 14 X M X 2(V -V1/2)/1000 X 100/m = 1.4 x M x 2(V-V1/2)/m

- The kjeldahl method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in the ring (e.g. pyridine) as nitrogen of these compounds does not change to ammonium sulfate under these conditions.

Q24) During the estimation of nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen, neutralized 10 mL of 1 M H_2SO_4. Find out the percentage of nitrogen in the compound.

Solution:

1 M of 10 mL H_2SO_4 = 1M of 20 mL NH_3 1000 mL of 1M ammonia contains 14g nitrogen

20 mL of 1M ammonia contains

$14 \times 20/1000$ g nitrogen

Percentage of nitrogen

$14 \times 20 \times 100/1000 \times 0.5 = 56\%$

iii) Halogens

(a) Carius method:

A known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as the Carius tube, in a furnace.

- Carbon and hydrogen present in the compound are oxidized to carbon dioxide and water.
- The halogen present forms the corresponding silver halide (AgX). It is filtered, washed, dried, and weighed.

1. **Let the mass of organic compound taken =** m g Mass of AgX formed = m1 g 1 mol of AgX contains 1 mol of X
2. **Mass of halogen in m1g of AgX =** atomic mass of X x m1g/molecular mass of AgX
3. **Percentage of halogen =** atomic mass of X x m1 x 100/ molecular mass of AgX x m

Q25) In the Carius method of estimation of halogen, 0.15 g of an organic compound gives 0.12 g of AgBr. Find out the percentage of bromine in the compound.

Solution:

Molar mass of AgBr = 108 + 80 = 188 g mol-1

188 g AgBr contains 80 g bromine

0.12 g AgBr contains 80 × 0.12/188 g bromine

Percentage of bromine = 80 × 0.12 × 100/188 × 0.15= 34.04%

iv) Sulfur

- A known mass of an organic compound is heated in a Carius tube with sodium peroxide or fuming nitric acid.
- Sulphur present in the compound is oxidised to sulphuric acid. It is precipitated as barium sulphate by adding excess barium chloride solution in water.
- The precipitate is filtered, washed, dried and weighed.
- The percentage of sulphur can be calculated from the mass of barium sulphate.

Let the mass of organic compound taken = m g

mass of barium sulphate formed = m1g

1 mol of $BaSO_4$ = 233 g $BaSO_4$ = 32 g sulphur

m1 g $BaSO_4$ contains 32 x m1/233 g sulphur

Percentage of sulphur= 32 x m1 x 100/23 x m

Q26) In sulphur estimation, 0.157 g of an organic compound gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound?

Solution:

Molecular mass of $BaSO_4$ =137+32+64=233g

233 g $BaSO_4$ contains 32 g sulphur

0.4813 g $BaSO_4$ contains 32 x 0.4813/233 g sulphur

Percentage of sulphur = 32 x 0.4813 x 100/233 x 0.157= 42.10%

(v) Phosphorus:

- A known mass of an organic compound is heated with fuming nitric acid whereupon phosphorus present in the compound is oxidized to phosphoric acid. It is precipitated as ammonium phosphomolybdate, $(NH_4)_3PO_4.12MoO_3$, by adding ammonia and ammonium molybdate.
- Alternatively, phosphoric acid may be precipitated as $MgNH_4PO_4$ by adding a magnesia mixture which on ignition yields $Mg_2P_2O_7$.

Let the mass of organic compound taken = m g and mass of ammonium phospho molybdate = m1g
Molar mass of $(NH_4)_3PO_4.12MoO_3$ = 1877g
Percentage of phosphorus = 31 × m1 × 100/1877 × m %
If phosphorus is estimated as $Mg_2P_2O_7$
Percentage of Phosphorus = 62 × m1 × 100/222 × m %

Where, 222 u is the molar mass of $Mg_2P_2O_7$, m the mass of organic compound taken m1, the mass of $Mg_2P_2O_7$ formed & 62 the mass of two phosphorus atoms present in the compound $Mg_2P_2O_7$

vi) Oxygen

The percentage of oxygen in a composition (100) and the sum of the percentages of all other elements.

Oxygen can also be estimated directly as follows:

- A definite mass of an organic compound is decomposed by heating in a stream of nitrogen gas.
- The mixture of gaseous products containing oxygen is passed over red-hot coke when all the oxygen is converted to carbon monoxide.
- This mixture is passed through warm iodine pentoxide (I_2O_5) when carbon monoxide as oxidized to carbon dioxide producing iodine.

$$\text{Compound} \xrightarrow{\text{heat}} O_2 + \text{other gaseous products}$$

$$2C + O_2 \xrightarrow[1373k]{} 2CO$$

$$I_2O_5 + 5CO \rightarrow I_2 + 5CO_2$$

The percentage of oxygen can be derived from the amount of carbon dioxide or iodine produced.
Let the mass of organic = mg
Compound taken
Mass of carbon dioxide = m1g
44g of carbon dioxide = 32g oxygen
m1 g carbon dioxide contains 32 × m1 × 100/44 × m %

- Presently, the estimation of elements in an organic compound is carried out by using microquantities of substances and automatic experimental techniques.
- The elements, carbon, hydrogen, and nitrogen present in a compound are determined by an apparatus known as CHN elemental analyzer.
- The analyzer requires only a very small amount of the substance (1-3 mg) and displays the values on a screen within a short time.

Most Important MCQs

Q1. Which of the following methods is best suited for the separation of a mixture containing naphthalene and benzoic acid

(a) Crystallisation
(b) Chromatography
(c) Sublimation
(d) Distillation

Answer (c)

Q2. Why do we boil the extract with conc. HNO_3 in Lassaigne's test for halogens?

(a) to increase the concentration of NO_3^- ions
(b) to increase the solubility product of AgCl
(c) it increases the precipitation of AgCl
(d) for the decomposition of Na_2S and NaCN formed

Answer (d)

Q3. Which type of isomerism is shown by propanal and propanone?

(a) Functional group
(b) Metamerism
(c) Tautomerism
(d) Chain isomerism

Answer (a)

Q4. Which of the following exhibits optical isomerism?

(a) Butanol-1
(b) Butanol-2
(c) Butene-1
(d) Butene-2

Answer (b)

Most Important MCQs

Q5. Find the compound which undergoes nucleophilic substitution reaction exclusively by an SN1 mechanism

(a) Benzyl chloride

(b) Chlorobenzene

(c) Ethyl chloride

(d) Isopropyl chloride

Answer (a)

Q6. How many structural isomers are possible if one hydrogen in diphenylmethane is replaced by chlorine?

(a) 8

(b) 4

(c) 7

(d) 6

Answer: (b)

Q7. The heterolytic bond dissociation energy of alkyl halides follows the sequence

(a) R – F > R – Cl > R – Br > R – I

(b) R – I > R – Br > R – Cl > R – F

(c) R – I > R – F > R – Br > R – Cl

(d) R – Cl > R – Br > R – I > R – F

Answer (b)

Q8. The shape of carbonium is

(a) Planar

(b) Pyramidal

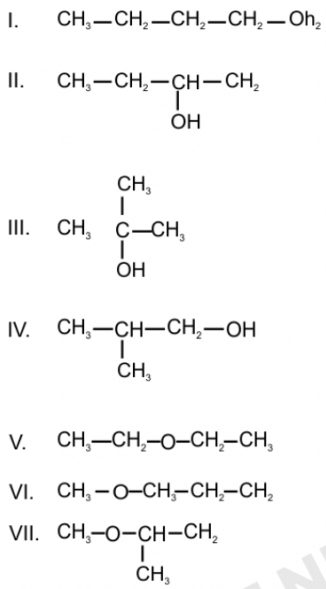
(c) Linear

(d) None of these

Answer (a)

Most Important Practice Problems

Note: Consider structures I to VII and answer questions 1-4.



Q1. Which of the above compounds form pairs of metamers?

Ans: If two or more compounds have the same molecular formula but different alkyl groups on either side of the functional groups then the compounds are said to be metamers.

In the given structures- V and VI and VI and VII form a pair of metamers because alkyl groups are different on either side of the functional groups.

Q2. Identify the pairs of compounds which are functional group isomers.

Ans: The compounds with the same molecular formula but different functional groups are said to be functional group isomers.

Alcohols are found to be the functional isomers of ether. In the given structures, the I, II, III, and IV alcohol functional group is present and V, VI, and VII contain an ether functional group. Hence, I and V, I and VI, I and VII, II and V, II and VI, II and VII, III and V, III and VI etc are functional group isomers.

Q3. Identify the pairs of compounds that represent position isomerism.

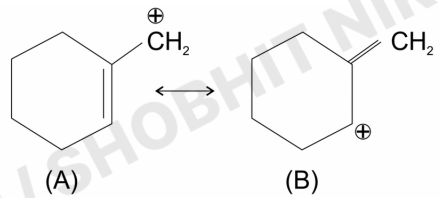
Ans: If two or more compounds differ in the position of substituent, functional group, or multiple bonds but the molecular formula is the same then these are said to be position isomers as they exhibit position isomerism.

Most Important Practice Problems

In the given structures, I and II, III and IV, and VI and VII are found to be the position isomers.

Q4. Identify the pairs of compounds that represent chain isomerism.
Ans: If two or more compounds have the same molecular formula but different carbon skeletons then these compounds are referred to as chain isomers and the phenomenon is termed chain isomerism. The pairs of compounds that represent chain isomerism are- I, II, III, and IV.

Q5. Which of the following ions is more stable? Use resonance to explain your answer.



Ans: Structure A is more stable than structure B. This is because carbocation A is more Planar and π electrons from the ring shift to the side group and are stabilized by resonance while structure B is non-planar and does not undergo resonance. Also, the double bond is more stable within the ring as compared to the side chain.

Q6. A liquid with a high boiling point decomposes on simple distillation but it can be steam distilled for its purification. Explain how is it possible.
Ans: Steam distillation is a special type of separation technique for temperature-sensitive materials such as natural organic compounds. Few organic compounds tend to decompose at higher temperatures and normal distillation does not fit this purpose. So, water is added to the apparatus and the temperature of the compounds is depressed, evaporating them at a lower temperature. Once the distillation is accomplished, the vapours are condensed and there occurs, and the separation of the constituents is at ease.

Most Important Practice Problems

Q7. Assertion (A): Sulphur present in an organic compound can be estimated quantitatively by the Carious method.
Reason (R): Sulphur is separated easily from other atoms in the molecule and gets precipitated as a light-yellow solid.
(i) Both A and R are correct, and R is the correct explanation of A.
(ii) Both A and R are correct, but R is not the correct explanation of A.
(iii) Both A and R are not correct.
(iv) A is not correct but R is correct.
Ans: Option (iii) i.e., Both A and R are not correct is the answer since sulphur is estimated by the Carius method in the form of a white precipitate of $BaSO_4$ on heating with fuming and $BaCl_2$. If a light yellow solid is obtained means impurities are present. It is filtered, washed and then dried to get pure $BaSO_4$.

Q8. Assertion (A): Pent- 1- ene and pent- 2- ene are position isomers.
Reason (R): Position isomers differ in the position of functional group or substituent.
(i) Both A and R are correct, and R is the correct explanation of A.
(ii) Both A and R are correct, but R is not the correct explanation of A.
(iii) Both A and R are not correct.
(iv) A is not correct but R is correct.
Ans: Option (i) i.e., Both A and R are correct, and R is the correct explanation of A is the answer as when two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are known as position isomers and this phenomenon is termed as position isomerism. Pent-2-ene and pent-l-ene are position isomers because they differ in the position of the double bond.

Q9. Identify the most stable species in the following set of ions giving reasons :

$$\overset{+}{C}H_3, \overset{+}{C}H_2Br, \overset{+}{C}HBr_2, \overset{+}{C}Br_2$$

Ans: In this case, CH3+ is the most stable species because the replacement of the H atom by the Br atom (-Inductive effect) increases the positive charge on the carbon atom and destabilizes the species.